Ammonia removal from swine wastewater using immobilized nitrifiers

Elimination en azote ammoniacal dans les lisiers de porcs en utilisant une technique d'immobilisation des nitrifiants.

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Abstract

Environmental pollution from animal waste is a major concern in the U.S.A. due to the rapid growth of confined animal production. This concern includes ammonia emissions, contaminated ground and surface water, and unexpected ecological shifts. Liquid swine manure is mostly treated and stored in large (0.25- to 5-ha) anaerobic lagoons before land application. For storage periods of 180 days typical of the Southeast, more than 50% of the nitrogen (N) entering the lagoon is lost by ammonia volatilization. Its subsequent deposition across the landscape may be the largest form of nitrogen non-point source pollution in the region. A possible solution is to remove ammonia through the transformation into N_2 using nitrification-denitrification systems. In order to overcome low nitrification rates in swine wastewater, we evaluated a new technology that uses immobilized nitrifying bacteria. The technology has been successfully applied to municipal wastewater treatment providing higher nitrification rates, shorter hydraulic residence times (HRT), and smaller reactors. Shorter HRT is critical for development of nitrification units to treat animal waste because aeration cost can be a limiting factor. Acclimated nitrifying cells were immobilized in 3- to 5-mm polyvinyl alcohol polymer pellets. Swine wastewater was treated in aerated, fluidized bioreactors with a 15% (w/v) pellet concentration using batch and continuous flow treatment. In batch treatment, 14 h were needed for total nitrification of ammonia-N (~250 mg N/L). In contrast, it took 10 d for a control (no-pellets) aerated reactor to start nitrification, and 69% of ammonia-N was lost by air stripping. In continuous flow treatment, ammonia removal efficiencies of more than 90% were obtained with ammonia loading rates of 418 mg N/L/d and HRT of 12 h. The rate of nitrification of swine wastewater obtained with HRT of 4 h was 604 mg N/L/d. The high nitrification rates obtained in this work indicate that the immobilized nitrifiers technology has potential application for reducing ammonia loss from confined animal production.

Keywords : ammonia removal, swine wastewater, nitrification treatment, immobilized nitrifiers.

Résumé

La pollution de l'environnement par les déjections animales est une préoccupation importante aux USA notamment à cause du développement de la production. Ces préoccupations concernent les émissions d'ammoniac, la contamination des eaux souterraines et de surface. Le lisier de porc est principalement stocké et traité dans de vastes lagunes anaérobies (0.25 à 5 ha de superficie) avant épandage sur les champs. Au cours de périodes de stockage de l'ordre de 180 jours, rencontrées dans le sud-est des Etats-Unis, plus de 50% de l'azote (N) entrant dans la lagune est perdu par volatilisation ammoniacale. Le dépôt ultérieur de cet azote à travers le paysage est peut être la principale forme de pollution azotée diffuse. Une solution possible consiste à éliminer l'azote ammoniacal à travers une transformation en azote moléculaire (N_2), en utilisant la nitrification-dénitrification. Afin de surmonter les faibles taux de nitrification obtenus habituellement dans les lisiers de porcs, une nouvelle technologie a été évaluée qui utilise les bactéries nitrifiantes immobilisées. Les cellules nitrifiantes ont été immobilisées dans des granulés (polymères). Le lisier de porc recevant 15% (poids / volume) de granulés a été traité par aération. Dans les séquences en discontinu 14 h ont été nécessaires pour obtenir une nitrification complète de l'azote ammoniacal ($\approx$ 250 mg N/L). Le temps nécessaire pour obtenir un début de nitrification dans le lisier témoin (sans granulés) était de 10 jours. En système en continu, le taux d'élimination d'azote ammoniacal s'établit à plus de 90% avec des charges de l'ordre de 418 mg N/L/j et un temps de rétention hydraulique de 12 h.

Ces taux de nitrification élevés témoignent que la technologie d'immobilisation des nitrifiants présente un potentiel d'application afin de réduire la pollution et les pertes ammoniacales.

Mots-clés : élimination N-ammoniacal, lisier porc, traitement par nitrification, nitrifiants immobilisés.

1. Introduction

During recent decades, animal production methods in the U.S.A. have undergone dramatic changes. The predominant trend has seen animal production changing from small, individual operations into large, confined, commercial enterprises. For example, the number of hog farms in the U.S.A. has dropped from 600,000 to 157,000 over the past 15 years. Yet, the country's inventory of pigs has remained almost the same (USDA, 1995). Most noticeable is the case of the swine industry in the state of North Carolina, where hog populations have increased from 3 million to more than 9 million in the last five years and where 97% of the production activity is concentrated in large operations. On the average, each of these operations has 5100 hogs and produces 45.2 Mg of collectable manure-N per year (Barker and Zublena, 1995; USDA, 1995). Typical facilities use flush or pit-recharge systems to remove manure from the confinement houses. The flushed waste is mostly treated and stored in large anaerobic lagoons (0.25 to 5 hectares) and later applied to cropland.

Anaerobic lagoons are designed to perform a significant reduction in the organic content of the flushed waste. Although the anaerobic digestion process can reduce 80% or more of the organic matter from these high-strength wastewaters, these open lagoon systems are not without significant adverse environmental impact. Specifically, organic N is converted to free ammonia (NH_3) with much of it volatilized from the lagoon's surface. It may be anticipated that in a lagoon of long-term retention, 50 to 80% of the N will escape to the atmosphere (Miner and Hazen, 1977; Muck and Steenhuis, 1982; Barrington and Moreno, 1995; Braum et al., 1997). Recent estimates of NH_3 emissions from swine lagoons in North Carolina indicate that about 30 Mg of NH_3 per day volatilizes from a total of 2,000 ha of lagoons (Crouse et al., 1997). Once in the air, the ammonia may diffuse down into the surrounding land, or be carried away by wind and diffuse down into soil and water several miles from the source. Hutchinson et al. (1972) showed that plants can also serve as sinks of significant quantities of NH_3 from the air even at low atmospheric concentrations. It is estimated that airborne pollution now accounts for about one-third of the 2,300 Mg of N that enter the Neuse River basin of the eastern U.S.A. each year (Hans Paerl, pers. comm.). These and other considerations, such as the potential for contaminated ground and surface waters, fish kills, and unexpected ecological shifts, provide ample reason for a greatly increased interest in controlling ammonia emissions from confined animal production.

2. Ammonia Removal Through Biological Nitrification-Denitrification Treatment

An efficient method to remove ammonia from animal lagoon wastewater is through on-farm biological nitrification-denitrification control processes. The effectiveness of such biological nitrogen removal processes depends on the ability of nitrifying organisms to oxidize NH_3 to nitrate (NO_3-N). Once in a nitrate form, the transformation into N_2 (or denitrification process) needs two conditions: a source of carbon and an anaerobic environment. These conditions are typically found in wetlands or liquid manure storage units. Using lagoon swine wastewater with a nitrification pretreatment, Rice and coworkers (1998) increased more than five times the N removal potential of constructed wetlands. Bernet and coworkers (1996) found that denitrification can also be carried out in the same tank used for anaerobic digestion of swine wastewater. Their results indicate that design of a practical process combining anaerobic digestion and denitrification coupled to a nitrifying reactor needs consideration of the carbon (C) to NO_3-N ratio in order to obtain complete nitrate reduction to molecular N.

The basic problem related to nitrification in wastewaters with a high content of organic carbon is the low growth rate of the nitrifying bacteria; the generation time of these microorganisms is about 15 hours. Compared to heterotrophic microorganisms, which have generation times of 20-40 minutes, the nitrifiers compete poorly for limited oxygen and nutrients and tend to be overgrown or washed out (Figueroa and Silverstein, 1992; Wijffels et al., 1993).

The nitrification of lagoon swine wastewater is an especially difficult process because of the very low numbers of nitrosomonas and nitrobacter usually found after anaerobic treatment (Blouin et al., 1989). Even when the oxygen supply is plentiful, an adaptation period is needed to reach a minimum bacteria concentration before effective nitrification. In the absence of enriched nitrifying populations, aerobic treatment of lagoons can potentially add to problems by stripping ammonia into the atmosphere, particularly if uncontrolled or excessive flow rates of air are used (Burton, 1992). To overcome these problems, we recently proposed the use of immobilized nitrifying cells in polymer pellets for enhanced nitrification of swine wastewater (Vanotti and Hunt, 1996). This is an attractive approach to biological ammonia removal as applied to animal systems because the capacity of the reactor can be increased by increasing the nitrifiers' retention time independent from the wastewater retention time.

3. Immobilization Technology

Advances in biotechnology using immobilization technology have shown that conditions can be modified to enhance the activity of specific microorganisms performing a desirable chemical process. The immobilization of microorganisms in polymer resins is a widely applied technique in drug manufacturing and food processing. The application for municipal wastewater treatment has been recently developed and tested in Japan (Tanaka et al., 1991; Takeshima et al., 1993), and there are currently several full-scale municipal wastewater treatment plants using this technology. This was the result of a 10-year comprehensive research project intended to solve wastewater treatment problems using biotechnology. Through the immobilization process, the nitrifying microorganisms are provided with a very suitable environment to perform at maximum effectiveness. The nitrifiers are entrapped in 3- to 5-mm pellets made of polymers that are permeable to NH_3, oxygen and carbon dioxide needed by these microorganisms, resulting in a fast and efficient removal of NH_3. Typical materials are polyethylene glycol (PEG) and polyvinyl alcohol (PVA); these pellets are functional for more than 10 years. Wastewater is treated in a nitrification tank equipped with a wedge-wire screen to retain the pellets and a whole-floor aeration system to ensure high oxygen transfer and appropriate fluidization. Pellet volume is usually 7 to 15% of the total reactor volume. Nitrification rate with this technology can be three times higher than those of the conventional activated sludge process (Tanaka et al., 1991). This is important when assessing the application of nitrification technologies for animal systems because construction and aeration cost can be limiting factors.

4. Immobilization of Acclimated Swine Wastewater Nitrifying Bacteria

Preparation of nitrifying culture. An active culture of acclimated swine wastewater nitrifying bacteria (ANB) was prepared from seed sludge obtained from an overland flow treatment field used for nitrification of anaerobic lagoon wastewater effluent. The seed sludge was diluted to a level of 0.62 g/L by an inorganic salts medium (Furukawa et al., 1993) using a fill-and-draw cultivation method. The NH_4-N concentration of the medium was fixed to 300 mg/L, and the pH was adjusted to 8.5 by addition of 1 *N* K_2CO_3 twice a day. The cells were harvested after 10 days of incubation at 35°C. The cultivation procedure yielded 1 g-MLSS/L with a nitrification activity of 7.06 mg NH_4-N/g-MLSS/h.

Immobilization technique. The ANB was concentrated by sedimentation to 58 g/L and immobilized by a PVA-freezing method. One unit of concentrated ANB was mixed on a weight basis with one unit of 20% (w/v) PVA-HC (100 % saponification, Kurare Co., Osaka)[1] warm aqueous solution at 45°C. The mixture was then poured into a plastic tray, and frozen for 16 h at -4°C. After fast thawing, immobilized ANB-pelletized cubes of 3-5 mm were prepared using a sharp blade. The immobilized pellets were washed with the inorganic medium under aeration until foaming by unpolymerized PVA stopped. Pellets were produced at a rate of 766-g (wet) or 875-ml pellets per 1000 g of ANB-PVA initial mixture and contained 37.9 mg ANB/g-pellet (wet).

Recovery culture. Recovery cultures of immobilized ANB were carried out by the fill-and-draw cultivation method during 2 d at 35°C using inorganic salts medium under a loading rate of 2.0-mg NH_4-N/g-pellet/d. Recovered immobilized ANB pellets with a nitrifying activity of 2.06-mg NH_4-N/g-pellet/d were used in subsequent batch and continuous experiments. The nitrifying activity of ANB after immobilization and recovery was 2.27-mg NH_4-N/g-MLSS/h, which is 32.1% of the activity before immobilization. This activity is similar to values of 1.74- to 2.11-mg NH_4-N/g-MLSS/h reported by Furukawa et al. (1993) using acclimated marine nitrifiers.

[1]Mention of trademark, proprietary product, or vendor does not constitute a guarantee or warranty of the product by the U.S. Dept. of Agriculture and does not imply its approval to the exclusion of other products or vendors that also may be suitable.

5. Nitrification of Swine Wastewater Using Batch Treatment

Batch experiments were conducted to elucidate conditions that optimize nitrification of lagoon wastewater. The reactors consisted of conic aeration tanks with air supplied from the bottom of the tanks to ensure full fluidization of nitrifying pellets. Average dissolved oxygen concentration was 7.7-mg O_2/L. Pellets were added at 15.3% (w/v) [17.5% (v/v)] pellet to total volume ratio. Temperature was controlled using a circulated water bath and heat regulator. All experiments were conducted at 30°C. The wastewater used was a lagoon effluent from a swine operation in Duplin County, North Carolina. It contained 233-mg NH_4-N/L, 250-mg TKN/L, and 0 nitrate and nitrite. Other characteristics were 200-mg TSS/L, 150-mg BOD_5/L, 1357-mg alkalinity/L, and a pH of 8.3.

Data in Fig. 1 identify inhibitory boundary conditions of NH_4^+ and NO_2^- oxidation of swine wastewater by immobilized nitrifiers. During NH_4^+ oxidation, there is a release of hydrogen ions that decreases the pH to an extent related to the buffering capacity of the system. The alkalinity concentration of the wastewater (1357-mg $CaCO_3$/L) was lower than the 1670 mg/L needed for complete oxidation of 233-mg NH_4-N/L (assuming 7.14-mg $CaCO_3$/mg NH_4-N). As the NO_2-N accumulated and the pH decreased during progression of nitrification, the free un-ionized nitrous acid (HNO_2) increased to a value (0.2 mg/L) that inhibited NH_4^+ oxidation. Addition of NaOH pulses at 12-15 h relieved this inhibition, and NH_4^+ oxidation was completed. On the other hand, oxidation of NO_2^-N was inhibited during the first 9 h and during the pH adjustment period when un-ionized (free) NH_3 levels were higher than 1 mg/L. These values are consistent with the benchmark nitrification work of Anthonisen et al. (1976). Their studies showed boundary concentrations of 0.2 to 2.8 mg/L for free nitrous acid inhibiting NH_4^+ oxidation, and 0.1 to 1.0 mg/L for free ammonia affecting the oxidation of NO_2-N.

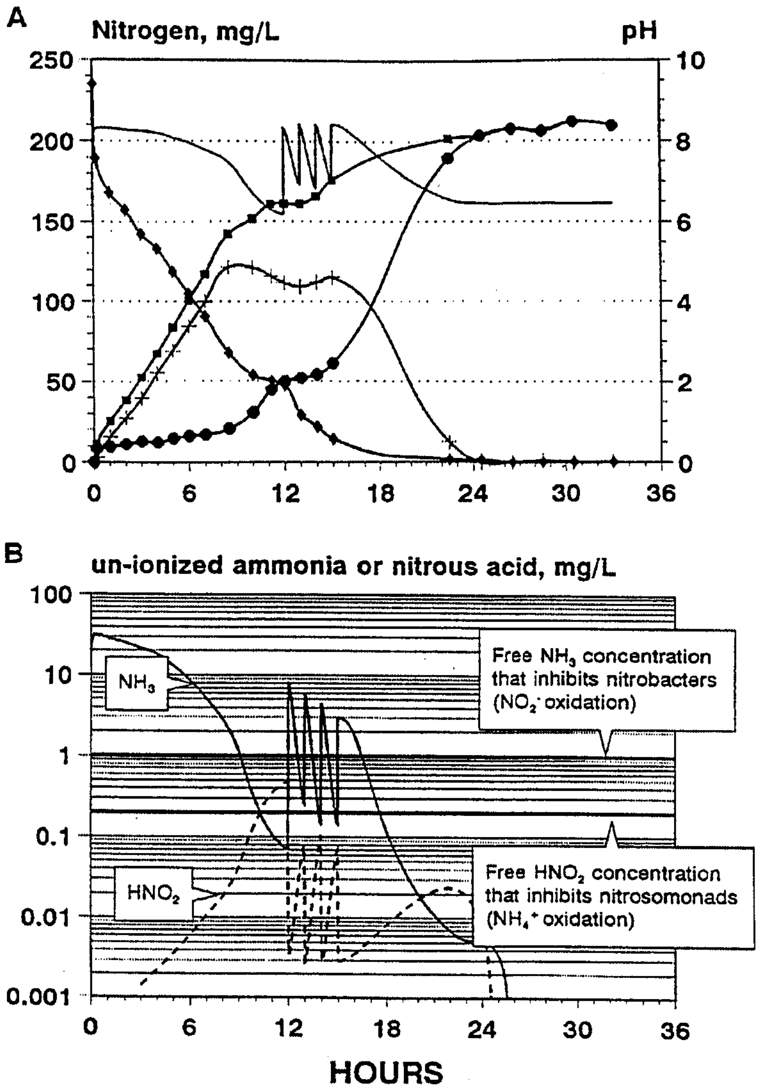

Figure 1

Nitrification of lagoon wastewater with immobilized nitrifiers, batch treatment.

***A:** Nitrogen transformations during inhibited nitrification; (◆) NH_4^+, (+) NO_2^-, (●) NO_3^-, (▪) NO_2^- plus NO_3^-, and (–) pH.*
***B:** Inhibitory boundary conditions of NH_4^+.and NO_2^-.oxidation.*

Inhibition of NH_4^+ oxidation by free nitrous acid can be easily relieved with pH control. Such a system is shown in Fig. 2; swine wastewater was supplemented with a pH 8.5 $CO_3^{=}/HCO_3^-$ buffer in order to add an extra 600 mg/L of alkalinity and meet H^+ demands of NH_4^+ oxidation. Under these conditions, NH_4^+ was completely oxidized in 14 h. But oxidation of NO_2-N was still inhibited by high initial free NH_3 in the lagoon wastewater; therefore, a total of 24 h was needed for complete nitrification to NO_3-N. This limitation is, however, an opportunity for bioengineering research through development of Nitrobacter strains adapted to higher levels of free NH_3, such as those acclimated to nitrify under harsh saline environments with free NH_3 concentration of 10 to 20 ppm (Furukawa et al., 1993).

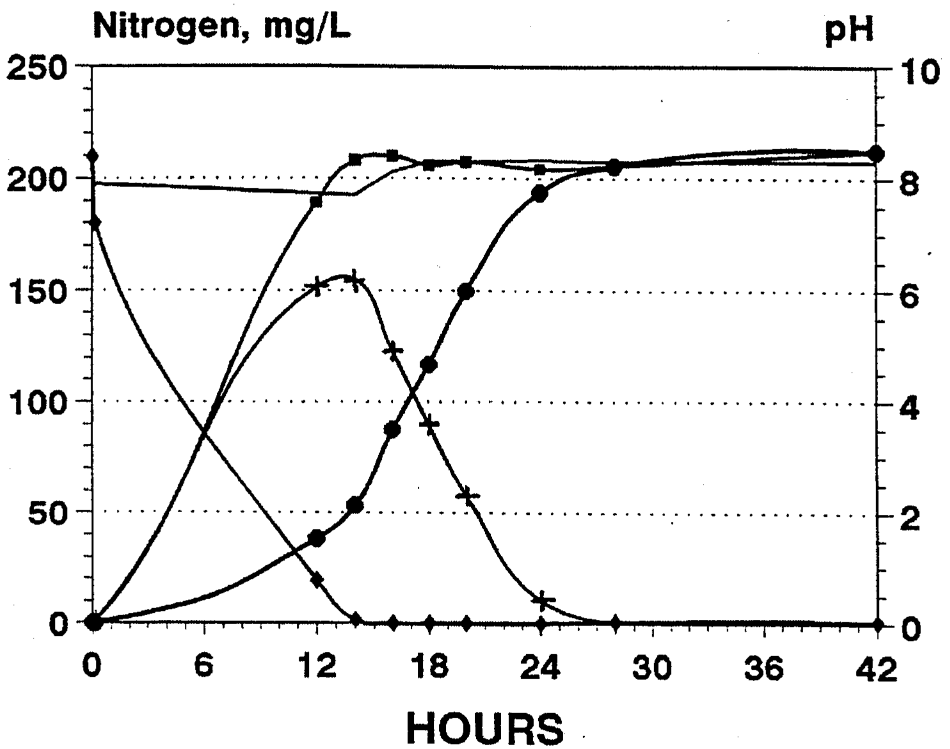

Figure 2
Nitrification of lagoon wastewater with immobilized nitrifiers in batch treatment using a $CO_3^{=}/HCO_3^-$ buffer for optimum process;
(◆) NH_4^+, (+) NO_2^-,(●) NO_3^-, (▪) NO_2^- plus NO_3^-, and (–) pH.

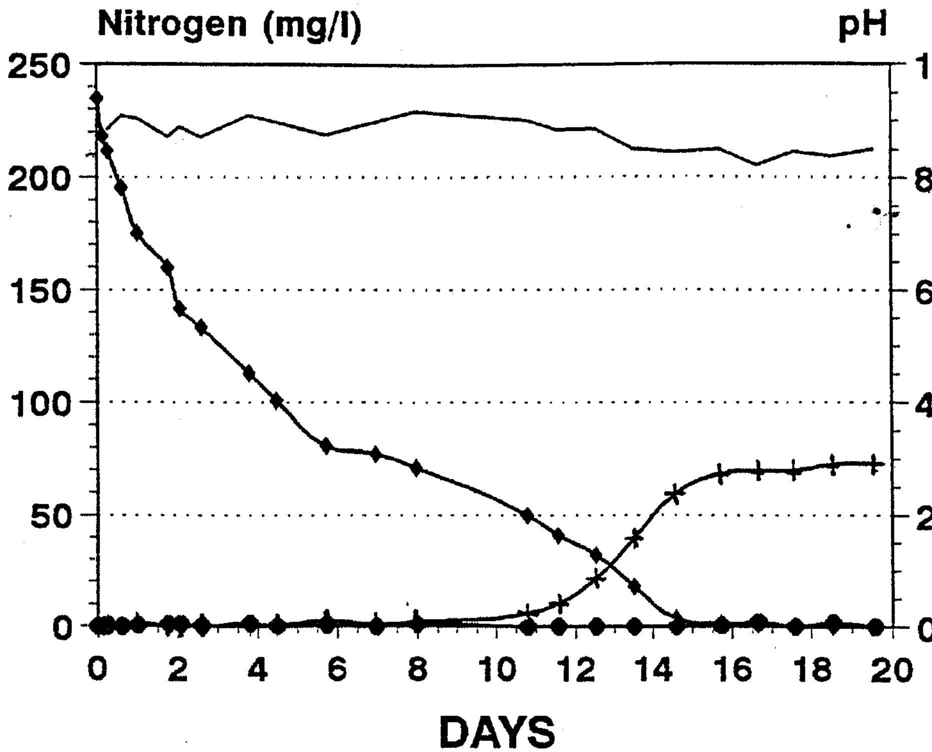

Figure 3
Nitrification of lagoon wastewater in a control batch treatment receiving only aeration,
without immobilized nitrifiers or pH correction;
(◆) NH_4^+, (+) NO_2^-,(●) NO_3^-, and (–) pH.

In the absence of enriched nitrifying populations, aerobic treatment of lagoons can potentially add to problems by stripping out ammonia. This problem is illustrated in Fig. 3, showing the nitrogen transformations in a control treatment that was conducted parallel to the experiment shown in Fig. 1. Nitrification of lagoon wastewater started at 10 d and 69% of NH_4^-N was lost by ammonia volatilization. These results are not surprising because of the low number of nitrifying microorganisms usually found after anaerobic stabilization (Blouin et al., 1989).

6. Nitrification of Swine Wastewater Using Continuous Flow Treatment

Ammonia removal potential of ANB pellets was also evaluated under continuous flow treatment. Ammonia loading rates were gradually increased from 227 to a maximum of 1287-g NH_4^-N/m^3 of aeration tank per day (corresponding from 1.48- to 8.40-mg NH_4^-N/g-pellet/d, respectively). Loading rates were changed by decreasing the hydraulic residence time (HRT) from 24 h to 4 h. Alkalinity requirements were corrected by adding an extra 600-mg alkalinity/L to the influent swine wastewater using a pH 8.5 $CO_3^=/HCO_3^-$ buffer. Pellets were retained inside the reactor with a 1-mm wedge-wire screen placed at the outflow. Other experimental conditions were similar to those described for the batch experiments.

HRT†	Ammonia Loading Rate	AmmoniaRemoval Rate‡	Nitrate + Nitrite Production Rate§	Nitrification Efficiency¶
hours	g N/m^3 reactor volume/day			%
24	227	223	240	100
20	260	254	279	100
16	326	311	327	100
12	418	363	397	95
8	637	402	417	65
6	884	498	499	56
4	1287	604	567	44

† Hydraulic residence time
‡ Ammonia removal rate = flow*(NH_4-N conc. inflow - NH_4-N conc. outflow)
§ NO_x-N production rate = flow*(NO_3-N+ NO_2-N conc. outflow); Inflow NO_X concentration=0
¶ Nitrification efficiency = (NO_X-N conc. outflow/NH_4-N conc. inflow)*100

Table 1
Treatment of lagoon swine wastewater with immobilized nitrifiers under continuous flow

Nitrification efficiencies of more than 90% were obtained with ammonia loading rates lower than 2.73-mg N/g-pellet/d and HRT higher than 12 h. Nitrification efficiencies decreased to 44% at the highest rate of 8.40-mg N/g-pellet/d (HRT = 4 h). All the ammonia-N removed was converted into nitrate and nitrite forms. Nitrate was predominant at HRT higher than 12 h, while equal amounts of nitrate and nitrite were produced at the highest load. Although higher loading rates resulted in lower nitrification treatment efficiencies, the total amount of NO_X^-N produced was higher, with the maximum ammonia removal rate obtained with HRT of 4 h. Higher efficiencies may be useful for total systems designed to meet stream discharge requirements. However, if the objective is to remove large amounts of ammonia from the lagoon, then a retrofit nitrification unit operated at shorter retention times would be recommended. This strategy has the advantage of reducing the total cost of aeration per unit of nitrate-N produced.

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